Facile Solvent-free Synthesis of Alkali Metal Dodecaborate $\text{M}_2\text{B}_{12}\text{H}_{12}$ ($\text{M} = \text{Li, Na, K}$)

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Supporting Information

Figure S1. XRD patterns of synthesized Na$_2$B$_{12}$H$_{12}$ compared with ICDD. (i) 5h ball milled 2NaBH$_4$ + B$_{10}$H$_{14}$ followed by heat treatment at 450 °C for 20 h (exposed in air for 1 min before measurement); (ii) 5h ball milled 2NaH + 1.2B$_{10}$H$_{14}$ followed by heat treatment at 450 °C for 20 h.
Figure S2. $^1$H MAS NMR spectra of synthesized samples from 2MBH$_4$ + B$_{10}$H$_{14}$ at different reaction conditions compared with MgB$_{12}$H$_{12}$ as reference (2LiBH$_4$ + B$_{10}$H$_{14}$: 5h ball milling, heat treatment at 200 °C for 15 h; 2NaBH$_4$ + B$_{10}$H$_{14}$: 5h ball milling, heat treatment at 450 °C for 20 h; 2KBH$_4$ + B$_{10}$H$_{14}$: 5h ball milling, heat treatment at 450 °C for 20 h). A peak at 4.8 ppm seen for Mg$_2$B$_{12}$H$_{12}$ is originated from crystalline water which would not be removed without decomposing the B$_{12}$H$_{12}$ anion.
Figure S3. XRD patterns of synthesized Li$_2$B$_{12}$H$_{12}$ using different routes and conditions compared with ICDD. (i) and (ii) are 5h ball milled 2LiH + 1.2B$_{10}$H$_{14}$ followed by heat treatment at 200 °C for 10 h and at 200 °C for 15 h; (iii) and (iv) are 5h ball milled 2LiBH$_4$ + B$_{10}$H$_{14}$ followed by heat treatment at 200 °C for 10 h and at 200 °C for 15 h; (v), (vi) and (vii) are LiH, LiBH$_4$ and B$_{10}$H$_{14}$ as reference.